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Structural and optical studies of Zinc doped TiO_2 nanoparticles

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Abstract
In the present work, Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 nanoparticles (NPs) were synthesized by solgel method. Crystalline size of the Zinc doped TiO_2 NPs were estimated by using DLS studies. X-ray diffraction patterns confirm the presence of anatase and rutile mixed phase of the synthesized NPs. The structural and morphological properties of the synthesized NPs were investigated by field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). Energy dispersive X-ray spectroscopy (EDX) analysis reveals presence of Ti, Zn and O elements in the synthesized NPs. The optical properties are studied by using UV-Vis absorption spectrum. The optical bandgaps of the synthesized NPs were calculated by using Tauc plot.

Keywords: *TiO_2 nanoparticles, solgel method, anatase phase, rutile phase, Optical properties.*

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I. Introduction

Titanium dioxide or Titania (TiO_2) is a transition metal oxide semiconductor having high band gap, high chemical stability and low production cost. It exists in both amorphous and crystalline forms. Anatase, rutile and brookite are the three crystalline phases of TiO_2. Among these three, anatase and rutile are most thermally stable phases than brookite [1]. In addition to that, mixed anatase and rutile phase exhibits an enhancement in the performance of the nanoparticles (NPs).

TiO_2 NPs has wide area of interest due to its unique technological properties and applications such as memory devices, sensors, photo catalysis and solar cells. It has been investigated as a prospective material for sensitized solar cells [2]. TiO_2 NPs absorb more amounts of sensitizers (Quantum dots or dye molecules), which results into the increase photon to current conversion efficiency [3]. In spite of these advantages, it absorbs insufficient amount of visible light because of its wide band gap, Hence the challenging issue is to improve the light harvesting capacity of the TiO_2 NPs. Recently, several reports reveal that the doping is the one of the typical approaches to overcome this limitation [4]. Dopants determine the optoelectronic properties of the materials. Among other depends, lattice distortion is small while doping Zn to TiO_2 because of the similar ionic size of Zn^{2+} [5].

In this paper, we reported the preparation of Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 nanoparticles (NPs) by solgel method. The structural and optical properties of the synthesized NPs were studied by using different characterization technique.

II. Experimental

2.1. Materials used

Titanium (IV) isopropoxide (TIP, 99%), Zinc (II) chloride ($ZnCl_2$, 99.9%), Methanol (> 99.5%), Ethanol (>99%) and Hydrochloric acid (100%) were purchased from Sigma Aldrich and used without further purification.

2.2. Synthesis procedure

Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 nanoparticles (NPs) were synthesized by solgel method. The synthesis procedure is as follows; 20ml ethanol was added to the 5ml of titanium (IV) isopropoxide (TiP) and stirred well at room temperature for 1h. 150ml double distilled water was added drop by drops in to the above solution and stirred at 80 ºC for 6h and allowed to stand without any disturbance to complete the gelation process. After aging for 24h, it was washed with methanol and acetone followed by the calcination was done at 500 ºC. Hence to obtain pure TiO_2 nanoparticles or Zinc doped (0wt%) TiO_2 NPs. For the preparation of Zinc doped (1wt%) TiO_2 NPs, 1wt% of $ZnCl_2$ was dissolved into 150ml double distilled water hydrochloric mixture was added drop by drops in to the TiP in ethanol solutions and stirred at 70 ºC for 6h and allowed to stand without any disturbance to complete the gelation process. After purification, this gel was calcinated at 500 ºC. Similar procedure was followed for the preparation of Zinc doped (2wt%) TiO_2 NPs also. Photographic representation of synthesis procedure of sol gel method is shown in Fig.1

Fig.1.Photographic representation for synthesis procedure of nanoparticles by sol gel method

1.3 Characterizations

X-ray diffraction (XRD) analysis was performed to find the crystal structure, crystallite phase and crystalline size of the synthesized NPs. It was performed by using Rigaku Ultima IV model X-ray diffractometer with Cu-Kα source over the scan range of 10-80 º. The dynamic light scattering (DLS) technique was performed by using Malvern instrument Ltd. (model No. MAL1043157). A field emission scanning electron microscope (Model: Zeiss Supra 55VP) was used to record FE-SEM image. High resolution transmission electron microscopy (HR-TEM) image was obtained by using FEI, USA, Tecnai G2-F30STwin model HR-TEM microscope. The elemental composition of the prepared nanoparticles was determined by energy-dispersive X-ray spectrometer (EDX) coupled with the HR-TEM microscope. UV-VIS spectrum was carried out by UV3600+ model Shimadzu UV-Vis spectrometer in the wavelength range of 200 to 800nm.

III. RESULTS AND DISCUSSION

3.1 XRD studies

Fig.2 shows the XRD patterns of Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs. Sharp and strong peaks in the XRD pattern indicates the crystalline nature of the synthesized NPs. The mixed anatase and rutile phase of TiO_2 NPs can be observed in the diffraction patterns of all the three samples. Peak marked 'A' and 'R' represents the anatase and rutile phase, respectively. The diffraction peaks at around $2\Theta = 25.2^o$, 37.9^o, 48.0^o, 53.8^o, 55.0^o, 62.8^o and 70.1^o, correspond to the (101), (004), (105), (211), (204), (126) and (220) planes of the anatase structure of TiO_2 (JCPDS 89-4921) [6,7]. The peaks at $2\Theta = 27.3^o$, 36.2^o, 39.2^o, $41.3\,^o$ and $58.8\,^o$ correspond to the (110), (101) (200), (111) and (210) planes of the rutile structure of $TiO_{2.}$ (JCPDS 21-1276) [3]. There is no additional peak corresponding to Zinc oxide was observed. Which indicate that doping of zinc does not change the tetragonal structure of $TiO_{2.}$ This is because of the similar ionic size of Ti^{4+} and Zn^{2+} [5,8]. But the intensity of anatase peaks is high in 0wt% Zinc doped TiO_2 NPs or pure TiO_2 NPs. It decreases with increase in Zn concentration. But the intensity of the rutile peaks increases with increasing the doping concentration. It indicates that, when the Zn^{2+} content is low, Zn^{2+} ions can exist as the O-Zn-Cl surface space; when Zn^{2+} content is high, the Zn^{2+} ion would form $ZnTiO_3$ species[8]. Hence, the increase in doping concentration of Zn^{2+} promote the formation of $ZnTiO_3$ it benefits the phase transformation from anatase to rutile [8]. The crystal size of the synthesized Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs is calculate by using the Scherrer formula $D=(k\lambda)/(\beta\cos\theta)$, where D is the crystalline size, k is the Scherer constant (0.9), β is the full width half maximum (FWHM) of the diffraction peak. ɵ is the Braggs angle of diffraction and λ is the wave length of X ray radiation (for Cu-Kα line, λ=1.54A^0) [9] and it is found to be 52.76nm, 49.05nm and 47.89nm, respectively.

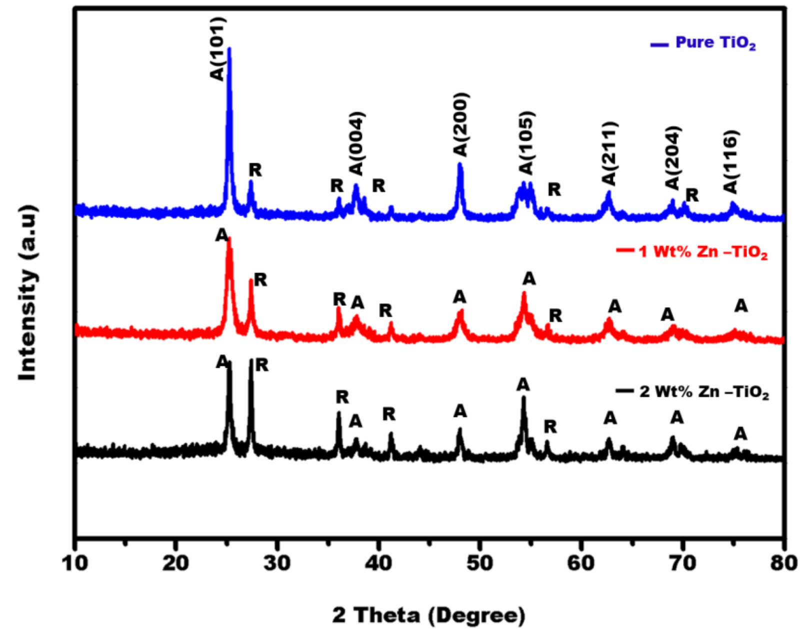

Fig.2 XRD pattern of Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs (A, anatase; R, rutile)

3.2 DLS studies

Dynamic light scattering (DLS) histogram of the doped (0wt%, 1wt% and 2wt%) TiO_2 NPs is shown in Fig.2. This result revealed that the average size of the 0wt% Zinc doped TiO_2 NPs or pure TiO_2 NPs is 53.92 nm and that of 1wt% Zinc doped TiO_2 NPs and 2wt% Zinc doped TiO_2 NPs are 51.23 nm and 49.08 nm, respectively. Decrease in crystalline size of NPs on Zn doping is due to the reduction in densities of the nucleation center [10].

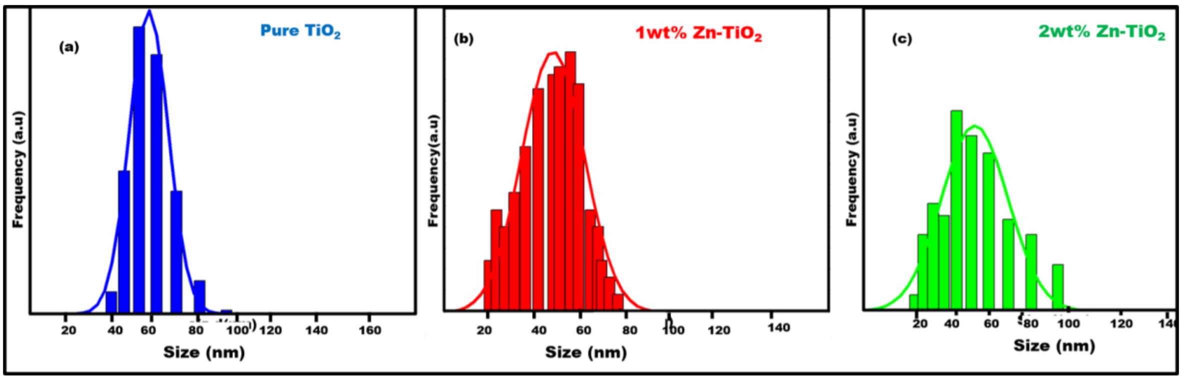

Fig. 3 DLS histograms of Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs

3.3 HR-TEM analysis

Fig. 3(a-c) depicts HR-TEM images of the synthesized Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs. Well defined lattice fringes are observed in the HRTEM images of synthesized NPs. This result confirms the crystalline nature of the NPs. All these three images, an average diameter of Zinc doped TiO_2 NPs was found to be at around 50 nm. It is very close to the crystallite size calculated from the Scherrer formula and DLS result. One of the lattice fringes observed in each HR-TEM images is 0.352 nm, which corresponds to the spacing distance of (101) planes of TiO_2 NPs [11]. Inset of inset of Fig.3 (a), (b) and (c) shows the selected area diffraction (SAED) patterns. Concentric rings are clearly visible in these SAED patterns. This result also confirms the crystalline nature of the synthesized NPs. The diameter of the rings in SAED patterns corresponds to (110), (101) (200) and (111) planes of TiO_2 NPs this firmly support the XRD result.

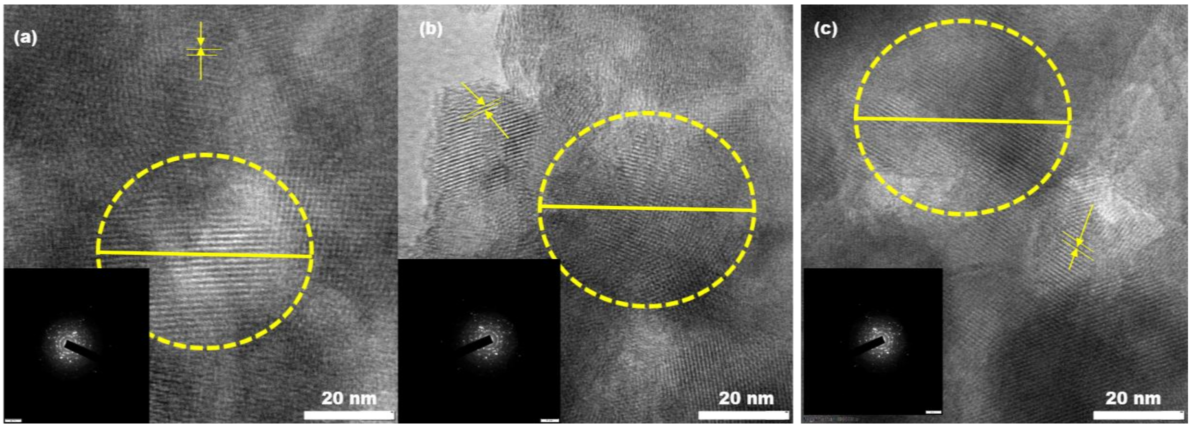

Fig .4(a) HR-TEM image of 0wt% Zinc doped TiO_2 NPs (b) HR-TEM image of 1wt% Zinc doped TiO_2 NPs and (c) HR-TEM image of 2wt% Zinc doped TiO_2 NPs

3.4 FE-SEM analysis

Fig. 4 (a-c) depicts FE-SEM images of the Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs. It shows the homogeneous spherical morphology of the synthesized NPs. It clearly indicates all samples contain the individual nanoparticles as well as a few numbers of aggregates. More agglomerations of the particles can be observed in Zinc doped (1wt% and 2wt%) TiO_2 NPs than that of undoped TiO_2 NPs,

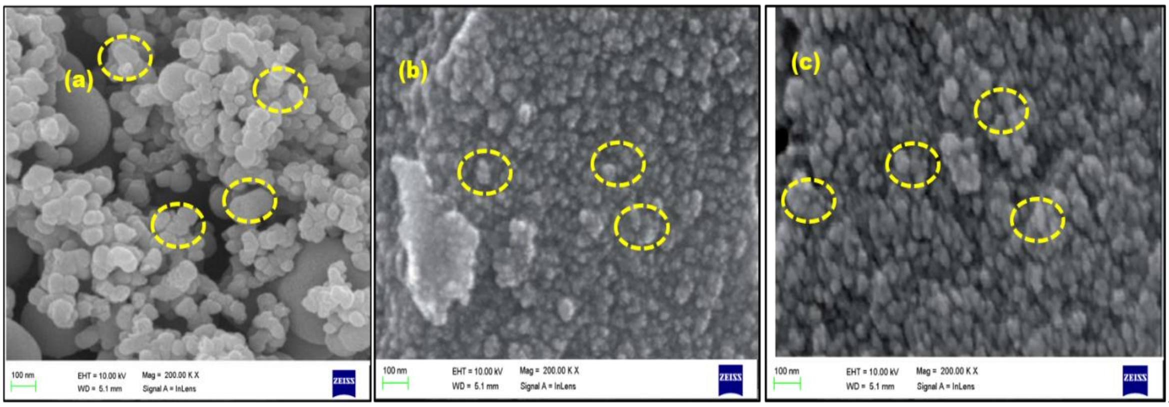

Fig .5 (a) FE-SEM image of 0wt% Zinc doped TiO_2 NPs (b) (a) FE-SEM image of 1wt% Zinc doped TiO_2 NPs (c) FE-SEM image of 2wt% Zinc doped TiO_2 NPs

3.5 EDX spectrum analysis

In order to confirm the elemental composition of the synthesized Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs, energy dispersive X-ray spectrums (EDX) are performed. Fig. 6 (a-c) shows the EDX spectra of synthesized NPs. Presence of titanium (Ti) and oxygen(O) elements was observed in Zinc doped 0wt% TiO_2 NPs (Fig.6 (a)). But in Zinc doped 1wt% and 2wt% TiO_2 NPs (Fig 6 (b) and (c)) presence of Zinc, Titanium and Oxygen elements are observed. More than that the elemental concentration of Ti is decreased with increasing doping concentration.

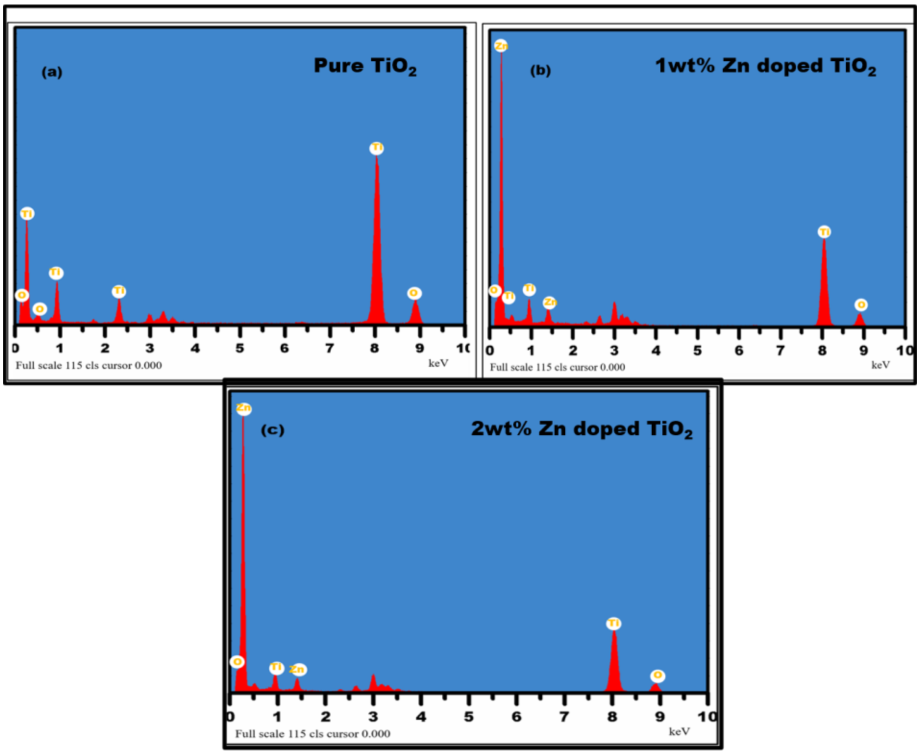

Fig.6 (a) EDX spectrum of 0wt% Zinc doped TiO_2 NPs (b) EDX spectrum of 1wt% Zinc doped TiO_2 NPs and (c) EDX spectrum of 2wt% Zinc doped TiO_2 NPs.

3.6 UV-Vis spectrum analysis

Fig.7 shows the UV-Vis absorbance spectrum of the synthesized NPs dispersed in chloroform. This spectrum shows that all of the samples exhibit continuous absorbance from the UV region to near-infrared region. Absorbance increases slowly with increasing the doping concentration with a slight red shift of onset position and absorption shoulder. For 2wt% Zn doped TiO_2 NPs has a high redshift of light absorbance with respect to pure TiO_2 NPs. This indicates that the 2wt% Zn doped TiO_2 NPs have high light-harvesting capacity than 0wt% Zn doped TiO_2 NPs. It is crucial for photovoltaic applications [12].

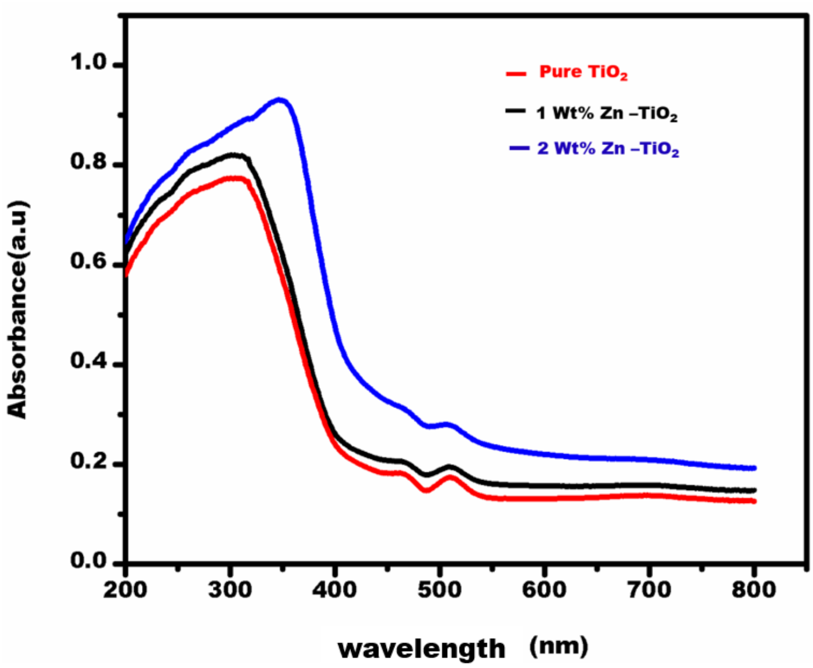

Fig.7 UV-Vis spectrum of Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs

The optical band gap of the synthesized NPs was estimated from the Tauc plot of UV-Vis spectra by plotting $(\alpha h\nu)^2$ Versus hν, using the relation [13].

$$\alpha h\nu^2 = A_o(h\nu - E_g)$$

where α represents the absorption coefficient, h is the planks constant, ν is the frequency, E_g is the band gap and A_o is the constant related to the effective masses associated with the bands. From linear extrapolation of the Tauc plot (Fig. 8), band gap value of Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs are determined to be 3.16, 3.07 and 2.96 eV, respectively. It indicates that 2wt% Zinc doped TiO_2 NPs has more light harvesting capacity than pure TiO_2 NPs and 1wt% Zinc doped TiO_2 NPs The reported bandgap energy of anatase TiO_2 NPs is 3.20 eV and that of rutile TiO_2 NPs is 3.02 eV [2,4,13]. The synthesized pure TiO_2 NPs has a bandgap very close to the bandgap energy of the anatase TiO_2 NPs and the bandgap energy of the other two nanoparticles (c) are very close to the bandgap energy of rutile TiO_2 NPs. This result revealed that the intensity of rutile peaks increases while doping. It supports the XRD result.

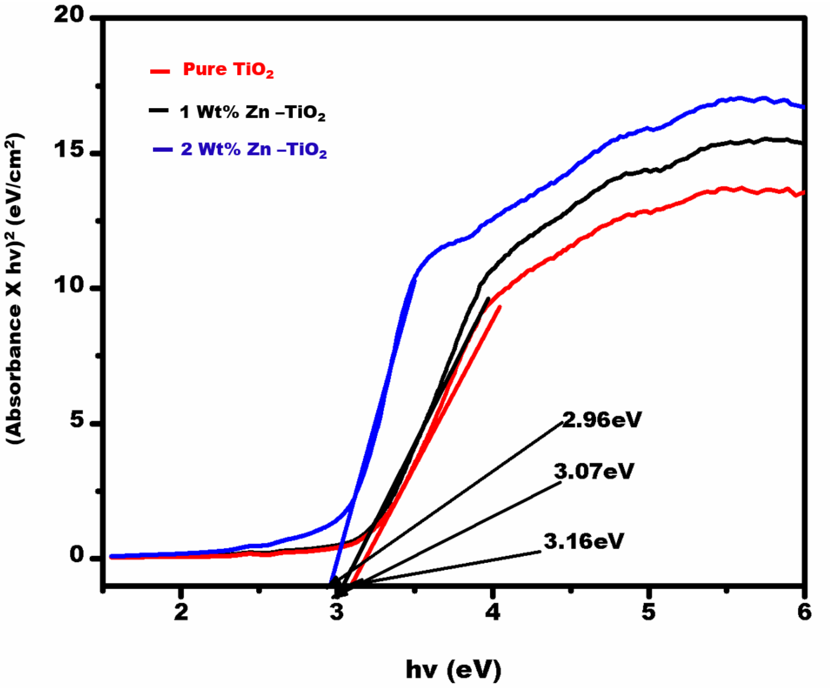

Fig. 8 Tauc plot of Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs

IV. Conclusion

Average diameters of about 50 nm Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs are synthesized by solgel method. The mixed anatase and rutile phase of TiO_2 NPs can be observed in the XRD diffraction patterns of all three samples. HR-TEM analysis confirms the crystalline nature of the synthesized NPs. EDX spectrum revealed the presence of Zn in the doped samples. UV-Vis absorbance spectrum shows that 2wt% Zn doped TiO_2 shows high light harvesting capacity than that of the other two NPs. From the Tauc plot, band gap of the synthesized Zinc doped (0wt%, 1wt% and 2wt%) TiO_2 NPs were determined and are found to be at 3.16, 3.07 eV and 2.96eV, respectively.

Conflict of Interest

The authors declare no competing financial interest.

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